



Surface reconstruction enabling MoO₂/MoP hybrid for efficient electrocatalytic oxidation of *p*-xylene to terephthalic acid

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ARTICLE INFO

Keywords:

Electrocatalytic oxidation
p-Xylene
Transition metal phosphide
Surface reconstruction
Terephthalic acid

ABSTRACT

Selective oxidation of *p*-xylene (PX) to terephthalic acid (TA) remains exceptionally challenging since it easily undergoes deep oxidation. Herein, a nickel foam-supported molybdenum dioxide/molybdenum phosphide hybrid electrocatalyst (MoO₂/MoP/NF) is reported for highly selective generation of TA via electrocatalytic oxidation (ECO) of PX in alkaline medium. The efficient MoO₂/MoP/NF anode material displays a unique cluster-like nanocone architecture, showing abundant active sites and rapid charge transfer kinetics. Benefit from the synergy between MoO₂ and MoP, the MoO₂/MoP/NF provides a high TA selectivity of 94.8% and an outstanding faradaic efficiency of 76.9% at the conversion of 71.6%. Additionally, the anodic oxidation of PX over MoO₂/MoP/NF promotes the cathodic hydrogen production. The potential-induced surface reconstruction of the as-synthesized MoO₂/MoP/NF yields new phases of phosphomolybdate and potassium molybdate. The top P site on the phosphomolybdate surface facilitates the adsorption of reaction intermediates but weakens the adsorption of TA, thereby yielding high selectivity toward TA.

1. Introduction

As the shortage of traditional energy and environmental pollution have become the major problems restricting economic and social development, it is very urgent to find pollution-free resources. Hydrogen is considered to be the most promising energy carrier to replace fossil fuels in the future due to its high energy density, abundant sources and sustainability [1]. Hydrogen production by water electrolysis based on renewable energies can not only obtain high purity products, but also reduce carbon emissions, which is in line with the strategy of sustainable [2,3]. However, anodic oxygen evolution reaction (OER) is a four-electron process with slow kinetics that leads to the actual voltage of water electrolysis much higher than the theoretical voltage (1.23 V), which has become a bottleneck limiting the development of hydrogen production by water electrolysis [4–7]. Up to now, replacing OER with a thermodynamically favorable electrocatalytic oxidation (ECO) of organics including alcohols [8,9], urea [10,11], hydrazine [12,13] and 5-hydroxymethyl furfural [14,15] not only reduces the anodic

overpotential, but also produces high value-added chemicals coupled with hydrogen production [16–18]. The expansion of new ECO systems coupled with hydrogen production for green synthesis of economically valuable organic compounds becomes a hot issue.

As an important chemical intermediate, terephthalic acid (TA) is usually obtained in industry through aerobic oxidation of *p*-xylene (PX) using Co-Mn-Br as the catalyst at 200 °C and 3.0 MPa in acetic acid [19]. Although the conversion of PX and the selectivity of TA are up to 90%, bromine corrodes equipment at high temperature and produces harmful by-products, resulting in high production costs and environmental pollution. Zhang et al. [20] developed an “out-slot type” indirect electrochemical method for the synthesis of TA using Cr₂O₇²⁻/Cr³⁺ as the redox pair in 5 M H₂SO₄ at 110 °C, giving the maximum TA yield of 78.5%. Such indirect electrochemical method involves concentrated acidic electrolyte, high reaction temperature and toxic catalyst, which lead to high equipment cost and environmental pollution. Raj et al. [21] performed the ECO of PX in an undivided electrolytic cell with an emulsion consists of CHCl₃ and 0.46 M H₂SO₄ containing 2% NaNO₃

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<https://doi.org/10.1016/j.apcatb.2023.123229>

Received 9 May 2023; Received in revised form 31 July 2023; Accepted 24 August 2023

Available online 25 August 2023

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($V_{\text{CHCl}_3}/V_{\text{H}_2\text{SO}_4} = 1/2$). Under the optimal experimental conditions, an 84% selectivity of *p*-tolualdehyde was obtained at the PX conversion of 88%. Up to now, most electrocatalytic methods on the synthesis of aromatic acids adopted aromatic alcohols as raw materials [9,22,23]. The selective electrocatalytic oxidation of $-\text{CH}_3$ to $-\text{COOH}$ has not been reported. In the oxidation of PX, high dissociation energy is required for the activation of inert C-H bond. The $-\text{COOH}$ group of TA is much easier to be oxidized with respect to the C-H bond of PX. Hence, it is still challenging to achieve high selectivity of TA owing to seriously deep oxidation [24]. Design of suitable electrocatalysts is highly desirable to realize the economically electrochemical method for TA production.

Transition metal phosphides have been widely employed in electrocatalysis due to their earth-abundance, remarkable catalytic activity and electrical conductivity [25–27]. Recent studies have established that surface reconstitution of transition metal phosphide-based precatalysts plays a decisive role on the catalytic performance via potential-induced evolution of crystalline phase structure, morphology as well as electronic valence state [28–30]. Qiu et al. [31] reported the reconstruction of Co-Fe phosphide precatalysts into amorphous Co-Fe hydroxide nanosheets under anodic potential. The etching effect caused by the leached phosphorus species promoted the oxidation of residual Co-Fe species for deeply bulk reconstitution. The amorphous Co-Fe catalysts with highly exposed active sites showed excellent OER activities (254 mV at 10 mA cm^{-2} and 292 mV at 100 mA cm^{-2}) and durability (15 days at 100 mA cm^{-2}). Tao et al. [32] prepared cactus-like NiCoP nanosheets for ECO of HMF to FDCA. The Co substitution could adjust the valence state of Ni, making the surface reconstruction of NiCoP to NiOOH more easily. The selectivity of FDCA was up to 99.6% at the conversion of 99.8%, giving the faradaic efficiency of 96.1%. Nevertheless, most studies focus on the transformation process of metal

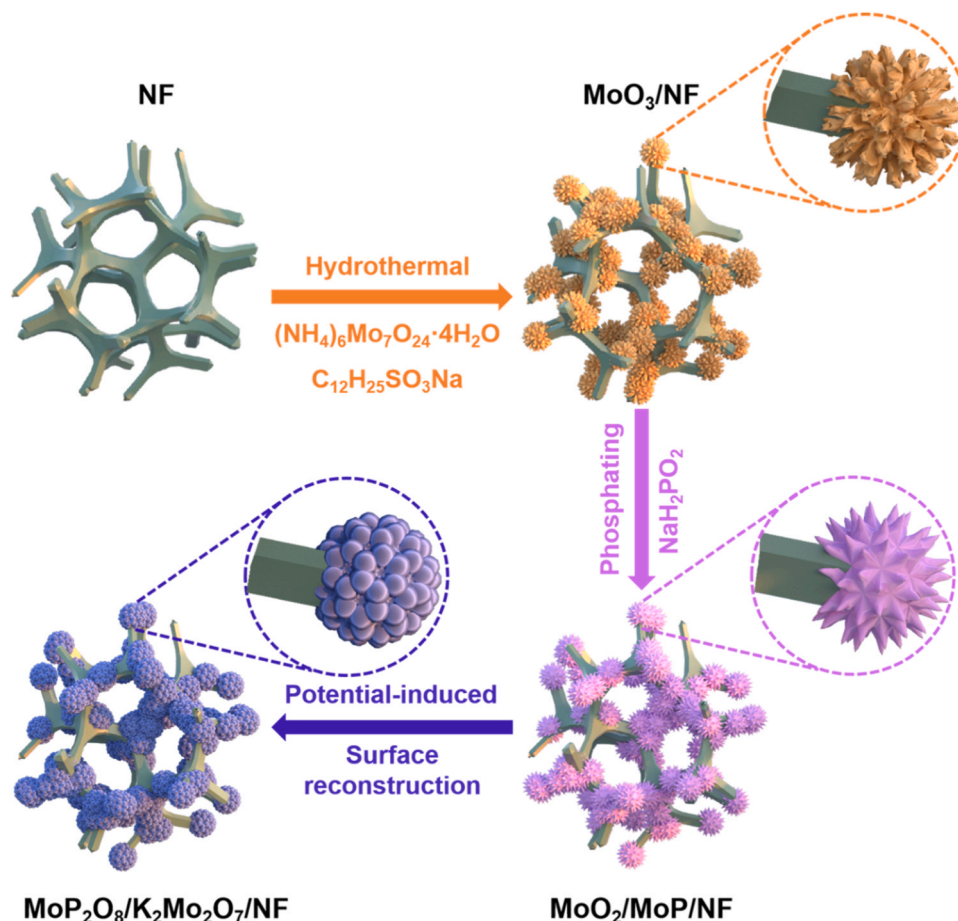
during surface reconstruction and subsequent oxidation reaction. The vital role of P remains elusive now.

In this work, we fabricated a nickel foam-supported hybrid precatalyst $\text{MoO}_2/\text{MoP}/\text{NF}$ by a facile two-step hydrothermal-phosphorylation method for selective oxidation of PX coupled with hydrogen production. The unique morphology endows the MoO_2/MoP electrocatalyst with large surface area and highly exposed active sites. The surface reconstruction of MoO_2/MoP into $\text{MoP}_2\text{O}_8/\text{K}_2\text{Mo}_2\text{O}_7$ facilitates moderate adsorption with intermediates but weak adsorption with TA, thereby yielding high selectivity toward TA. The $\text{MoO}_2/\text{MoP}/\text{NF}$ anode material not only manifests outstanding selectivity for TA, but also promotes the hydrogen production through coupling the cathodic hydrogen evolution with anodic PX oxidation. This work paves a promising pathway to achieve efficient ECO process via adjusting the dynamic active center based on potential-driven surface reconstitution of transition metal phosphide.

2. Experimental

2.1. Preparation of $\text{MoO}_2/\text{MoP}/\text{NF}$ electrodes

The $\text{MoO}_2/\text{MoP}/\text{NF}$ electrodes were prepared via a hydrothermal reaction followed by a phosphorylation process depicted in Scheme 1. Firstly, a piece of nickel foam (NF, $1.5 \times 3 \text{ cm}^2$) was soaked with 3 M hydrochloric acid for 15 min and then washed with deionized water and ethanol to remove surface impurities. Subsequently, 20 mM $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ and 100 mM $\text{C}_{12}\text{H}_{25}\text{SO}_3\text{Na}$ were added to 20 mL deionized water. After vigorously stirring for 30 min, the treated NF was put into the above solution. Then, the mixture was transferred to a 50 mL teflon-lined reactor and treated at different hydrothermal



Scheme 1. Schematic illustration for the synthesis procedure and morphological evolution of $\text{MoO}_2/\text{MoP}/\text{NF}$.

temperature for 12 h. After the reactor was cooled to room temperature, NF was washed with ethanol and deionized water, and subsequently dried at 80 °C for 12 h to obtain MoO₃/NF-x (x represents the hydrothermal temperature; x = 100 °C, 120 °C, 140 °C, 160 °C, respectively). Finally, the MoO₂/MoP/NF-x electrodes were obtained by calcining MoO₃/NF-x at 600 °C for 2 h under argon atmosphere with 2.5 g NaH₂PO₂.

The MoO₂/NF electrodes and MoP/NF electrodes were also prepared as controls. The experimental details were described in the [supplementary information](#).

2.2. Electrochemical measurements

The electrochemical measurements were depicted in the [supplementary information](#).

2.3. Electrocatalytic oxidation of p-xylene

ECO of PX was conducted on a IT7620 DC power supply using an H-type electrochemical cell. The anodic electrolyte contained 25 mM PX dissolved in 1 M KOH solution ($V_{H_2O}/V_{CH_3CN} = 7/3$). The cathodic electrolyte was 1 M KOH aqueous solution. The area of MoO₂/MoP/NF submerged in the electrolyte was set as $1 \times 3 \text{ cm}^2$. PX was quantitatively analyzed by gas chromatography (GC, Shimadzu). The oxidized products were detected by high performance liquid chromatography-mass spectrometry (HPLC-MS, Agilent). Further product analysis conditions were provided in the [supplementary information](#). The conversion (%), selectivity (%) and faradaic efficiency (%) were calculated as follows:

$$\text{Conversion (\%)} = \frac{\text{moles of PX consumed}}{\text{moles of initial PX}} \times 100\%$$

$$\text{Selectivity (\%)} = \frac{\text{moles of product}}{\text{moles of PX consumed}} \times 100\%$$

$$\text{Faradaic efficiency (\%)} = \frac{e n F}{Q} \times 100\%$$

where e is the number of electrons transferred during the oxidation of PX to TA ($e = 12$), n is the mole of TA produced, F is the Faraday constant (96,500 C/mol) and Q is the total electrons passed. The moles of substances were calculated from the concentration obtained by the standard curve (Figs. S1–S5).

2.4. Physicochemical characterizations

The details of physicochemical characterizations were presented in the [supplementary information](#).

2.5. Density functional theory (DFT) calculations

The details of DFT calculations were provided in the [supplementary information](#).

3. Results and discussion

3.1. Hybrid MoO₂/MoP/NF with cluster-like nanocone structure via hydrothermal- phosphorylation process

The MoO₂/MoP/NF-x precatalysts were prepared by a hydrothermal treatment followed by a phosphorylation process (Scheme 1). After the hydrothermal treatment at 100 °C, the XRD peaks match well with monoclinic MoO₃·2 H₂O (PDF#16-0497) (Fig. S6) [33]. With the increase of hydrothermal temperature, the hexagonal MoO₃ (PDF#21-0569) [34] becomes distinguishable. All the samples obtained at high hydrothermal temperature (above 120 °C) exhibit two distinct crystalline phases with good crystallinity including hexagonal MoO₃ and monoclinic MoO₃·2 H₂O. Moreover, the average crystallite sizes evaluated by Scherrer's equation progressively increase with increasing the hydrothermal temperatures (Table S1). Raman spectra (Fig. S7) of all the samples exhibit four characteristic peaks at 285, 339, 810 and 992 cm⁻¹, respectively. The peaks at 285 and 339 cm⁻¹ belong to the

O=M=O wagging (B_{2g} vibrational mode) and O-M-O bending (A_g vibrational mode) of MoO₃, while the peaks at 810 and 992 cm⁻¹ are attributable to the M=O stretching (A_g vibrational mode) of MoO₃ [35, 36]. So, it is demonstrated the formation of MoO₃ after hydrothermal treatment.

The temperature-dependent crystalline phases and structural features of MoO₂/MoP/NF-x were also disclosed by XRD and Raman spectra. After phosphorylation, the MoO₂/MoP/NF-100 shows a dominant crystalline phase of monoclinic MoO₂ (PDF#32-0671) [37–39] with trace hexagonal MoP (PDF#24-0771) [40] (Fig. 1a). As the hydrothermal temperature continues to increase, the hexagonal MoP becomes more pronounced. Notably, the as-prepared samples display both monoclinic MoO₂ and hexagonal MoP phases with good crystallinity at high hydrothermal temperature (above 120 °C). After the phosphorylation process, the as-obtained MoO₂/MoP/NF exhibits smaller crystallite size relative to the corresponding MoO₃/NF (Table S2), which might be attributed to the changes of crystalline phases during the phosphorylation process [41,42]. Similar changes were also found in Raman spectra (Fig. 1b). The characteristic bands located at 401 and 743 cm⁻¹ are consistent with the features of MoP and the Mo-O stretching vibration of MoO₂ [43,44]. Accordingly, it can be deduced that MoO₃ converts to MoO₂ and MoP in the presence of PH₃ and H₂ generated from NaH₂PO₂ decomposition [45].

The chemical valence states for the samples after hydrothermal and phosphorylation were analyzed by XPS. After hydrothermal reaction (Fig. S8), the B.E.s of Mo 3d at 235.47 and 232.31 eV are responsible for the Mo (VI) oxidation state of MoO₃ [46]. The high-resolution XPS spectra for O 1s show two peaks at 530.34 and 532.25 eV respectively, which can be derived from Mo (VI)-O of MoO₃ and O_{H2O} (adsorbed water) [47]. After phosphorylation (Figs. 1c-e, S9–S11), the high-resolution XPS spectra of Mo 3d can be fitted into five peaks. The peaks at 228.29, 229.63 and 232.25 eV correspond well to Mo^{δ+} species of MoP, Mo (IV) and Mo (VI) species respectively, indicating the coexistence of MoP and MoO₂ with partially oxidized surface [48,49]. The high-resolution O1s spectra exhibit three peaks at 531.08, 532.57 and 533.31 eV, which originate from the Mo(IV)-O bond from MoO₂, P-O and P = O bonds [48]. The B.E. of P 2p at 129.72, 130.70 and 133.89 eV can be assigned to P^{δ-} of MoP and P-O of PO₄³⁻, respectively [44]. It is evident that MoO₃ transforms into hybrid MoO₂/MoP during the phosphorylation process. As compared to other samples (Table S3), XPS analysis demonstrates that MoO₂/MoP/NF-140 has the lowest MoO₂/MoP surface ratio (3.1:1), which means that MoO₂/MoP/NF-140 has the highest proportion MoP.

The morphologies and structural features of as-prepared samples were characterized using SEM and TEM. Initially, MoO₃ nanorods with cone-like structures and rough surfaces were sparsely grown on the surface of NF skeleton at 100 °C (Figs. S12, S13a-b). As the hydrothermal temperature increases to 120 °C, nanocones aggregate into large clusters (Fig. S13c-d). At 140 °C, nanocone clusters become more densely and homogeneously distribute on the NF surface (Fig. S13e-f). However, with the hydrothermal temperature up to 160 °C, the stacked nanosheet-like structures can be observed in addition to nanocone clusters (Fig. S13g-h). After phosphorylation at 140 °C (Figs. 2a-b, S14), the three-dimensional architecture of cluster-like nanocone maintains whereas the rough surface becomes smooth. Such cluster-like nanocone architecture can expose abundant active sites that are easily contacted by reactants.

The MoO₃/NF-140 displays the lattice spacing of 0.315 and 0.191 nm respectively as revealed by HRTEM, which are indexed to the (334) plane of MoO₃ and the (404) plane of MoO₃·2H₂O. The specific features of the sample with the (334) plane of MoO₃, the (424) plane and (404) plane of MoO₃·2H₂O are revealed by the SAED pattern (Fig. S15). For the MoO₂/MoP/NF-140, the lattice spacing of 0.206 and 0.239 nm can be precisely assigned to the (–211) planes of MoO₂ and the (101) plane of MoP (Fig. 2c-e) [38,40]. The SAED pattern further verifies that the sample is composed of crystalline MoO₂ and MoP (Fig. 2f). The

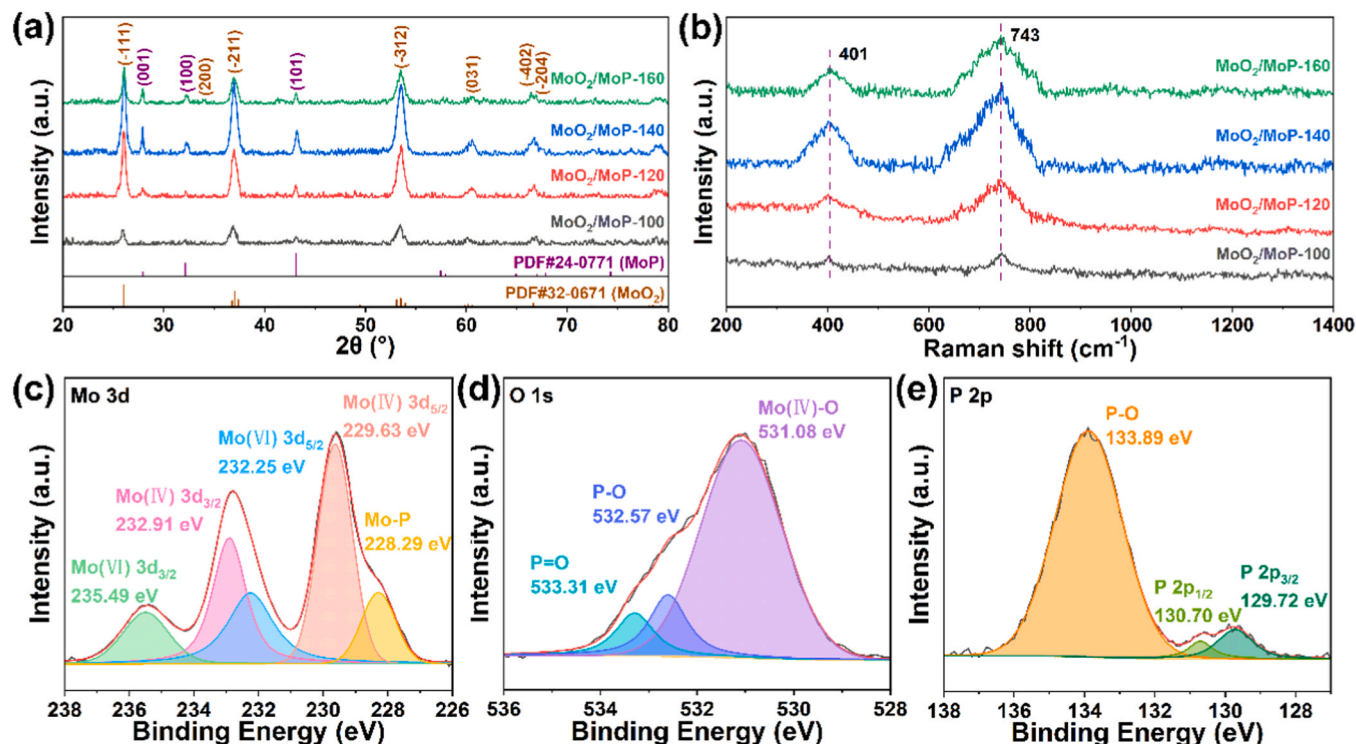


Fig. 1. (a) XRD patterns and (b) Raman spectra of as-prepared samples (the samples were scraped from NF for the XRD and Raman measurements). High-resolution XPS spectra for MoO₂/MoP/NF-140. (c) Mo 3d, (d) O 1s, (e) P 2p.

corresponding elemental mapping verify that Mo, O and P uniformly distribute on the MoO₂/MoP/NF-140 (Fig. 2g-j). So, it is demonstrated that MoO₂/MoP/NF electrode materials with large surface areas and highly exposed active sites can be obtained via a simple hydrothermal-phosphorylation method.

As a control, the structure and morphology of the MoO₂/NF-140 were also investigated. The MoO₂/NF-140 obtained by a hydrothermal-calcining procedure shows a typical crystalline phase of monoclinic MoO₂ (PDF#32-0671) (Fig. S16). It can be seen that small rectangular nanoparticles aggregate to form large clusters (Fig. S17). The lattice spacing of MoO₂/NF-140 (0.205 nm) matches well with the (111) plane of MoO₂. In addition, the corresponding elemental mapping shows the uniform distribution of Mo and O in MoO₂/NF-140 (Fig. S18).

3.2. Electrocatalytic oxidation of PX with high selectivity of TA

The ECO of PX utilizing MoO₂/MoP/NF electrodes under different conditions were presented in Fig. 3 and Table S4. The MoO₂/MoP/NF exhibits considerably higher TA selectivity (94.8%) as compared to other catalysts including NF (4.4%), commercial MoP/NF (5.8%) and MoO₂/NF (40.0%), implying a synergistic effect of MoO₂ and MoP in the ECO process of PX (Fig. 3a). Regarding the hydrothermal temperature adopted for MoO₂/MoP/NF, the conversion of PX shows no obvious difference. However, the selectivity of TA is highly dependent upon the hydrothermal temperature, and reaches to the highest value at 140 °C, followed by an apparent decrease at 160 °C (Fig. 3b). As a result, the MoO₂/MoP/NF-140 possesses the optimal TA selectivity of 94.8% at the PX conversion of 71.6%. HPLC-MS (Fig. S19, S20) analysis unveils the reaction pathway of ECO of PX, which involves a series of oxidation intermediates of *p*-tolualdehyde (*p*-TALD), *p*-toluic acid (*p*-TA), 4-carboxybenzaldehyde (4-CBA) and terephthalic acid (TA) (Fig. 3c). *p*-TALD, *p*-TA and 4-CBA are the major products within the initial 2 h, which shows descending *p*-TALD and ascending *p*-TA and 4-CBA. TA occurs at 3 h and becomes the dominant product after 4 h. Its selectivity progressively grows within 3–6 h. Accordingly, the reaction pathway for

ECO of PX over MoO₂/MoP/NF-140 was provided in Fig. 3d.

With the applied potentials stepping from 1.4 to 1.6 V vs RHE, both the conversion of PX and the selectivity of TA gradually ascends, accompanied by the decreased selectivity for *p*-TA and 4-CBA. The ECO of PX achieves the highest TA selectivity of 93.5% at 1.6 V vs RHE, giving the PX conversion of 73.8% (Fig. 3e).

Moreover, operating current density was also optimized (Fig. 3f). The ECO of PX exhibits the best performance at 10 mA cm⁻² since it undergoes apparent over-oxidation at high current density. The faradaic efficiency reaches up to an outstanding 76.9% under the optimal conditions (Fig. S21). As summarized in Table S5, it can be clearly seen that the MoO₂/MoP/NF electrode material achieves superior TA selectivity to other electrocatalysts and most of the reported catalysts in thermocatalysis and photocatalysis.

The cathodic hydrogen production was measured via a drainage method under ECO and OER conditions respectively [50] (Figs. 3g, S22). The hydrogen amount coupling with ECO of PX (13.5–14 mL/h) is higher than that under OER condition (9–10 mL/h), which indicates that the MoO₂/MoP/NF-140 could promote the hydrogen production by replacing OER with ECO.

The superiority of ECO to OER was further corroborated by electrochemical measurements. LSV profiles (Fig. 4a-b) demonstrate that the MoO₂/MoP/NF-140 exhibits obviously lower overpotential at 10 mA cm⁻² with PX (123 mV) than that without PX (148 mV). This difference becomes more significant at high current density, which proves that the MoO₂/MoP/NF-140 is preferential to drive ECO of PX rather than OER. Particularly, the MoO₂/MoP/NF-140 affords a considerably smaller Tafel slope of 39.8 mV dec⁻¹ with PX added relative to OER (60.8 mV dec⁻¹), which is indicative of a favorable reaction kinetics for the ECO of PX. Furthermore, a two-electrode hybrid water electrolysis system using MoO₂/MoP/NF-140 as the anode and Pt/C as the cathode were constructed to test the overall performance. LSV curves display that the PX electro-oxidation assisted water electrolysis (87 mV at 10 mA cm⁻²) exhibits lower overpotential than traditional water electrolysis (101 mV at 10 mA cm⁻²) at the same current density

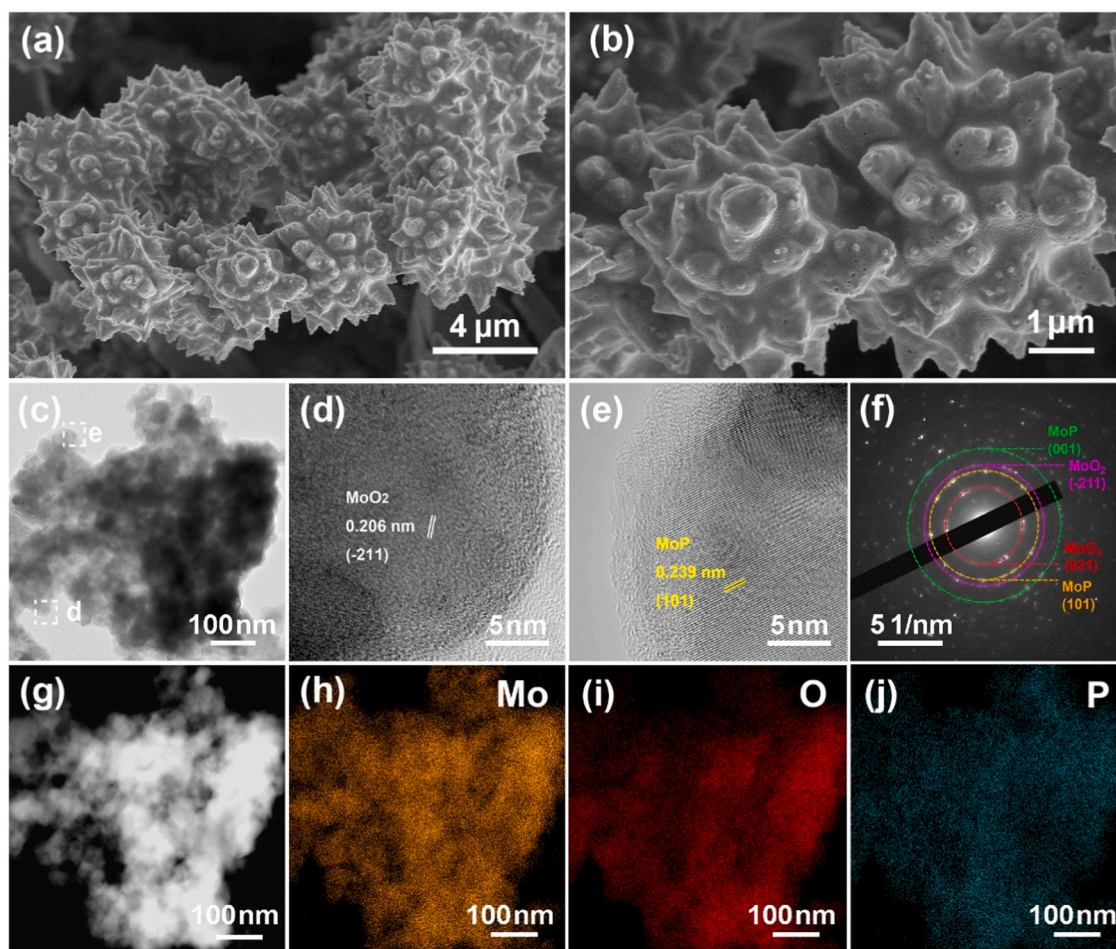


Fig. 2. (a, b) SEM images; (c) TEM image, (d, e) HRTEM images, (f) SAED pattern and (g-j) the corresponding TEM elemental mapping of MoO₂/MoP/NF-140.

(Fig. S23a). Significantly, PX electro-oxidation assisted water electrolysis requires only 1.42 V to drive 10 mA cm⁻² and possesses a superior stability with a negligible deactivation over 40 h (Fig. S23b). Comparing with other molybdenum-based catalysts for electrochemical organic compound oxidation, the MoO₂/MoP/NF-140 exhibits excellent ECO performance (Table S6).

Fig. 4c-d display LSV curves and Tafel slopes of MoO₂/MoP/NF-x electrodes synthesized at different hydrothermal temperatures. The MoO₂/MoP/NF-140 presents the overpotential of 123 mV (10 mA cm⁻²) and Tafel slope of 39.8 mV dec⁻¹ (Table S7), which is significantly smaller than those of MoO₂/MoP/NF-100 (137 mV, 52.4 mV dec⁻¹), MoO₂/MoP/NF-120 (133 mV, 48.4 mV dec⁻¹) and MoO₂/MoP/NF-160 (128 mV, 41.8 mV dec⁻¹). As compared to other electrode materials, the MoO₂/MoP/NF-140 possesses lower overpotential at the same current density after normalization by BET surface area (Fig. S24), demonstrating its higher intrinsic activity. Moreover, the MoO₂/MoP/NF-140 shows the highest C_{dl} value (82.5 mF cm⁻²) as compared to other electrodes, thus reflecting that it exposes abundant active sites (Figs. 4e, S25) [51,52]. Furthermore, the MoO₂/MoP/NF-140 exhibits the lowest charge transfer resistance (*R*_{ct}, 17.27 Ω) among all the tested electrodes, reflecting an efficient electron transfer (Fig. 4f, Table S7) [53]. From XRD, Raman and SEM results, the electrode materials prepared at low hydrothermal temperature (below 120 °C) are covered with cone-like nanorods with poor crystallinity. However, the morphology changes significantly at high temperature (160 °C), which would lead to small surface area. The MoO₂/MoP/NF-140 has good crystallinity and large surface area, thereby providing excellent electrochemical performance.

As compared to MoO₂/NF, MoP/NF and NF, MoO₂/MoP/NF shows

superior ECO activity with the lowest overpotential at 10 mA cm⁻², the lowest Tafel slope, the largest ECSA and the smallest *R*_{ct} (Figs. S26, S27, Table S8), demonstrating a synergistic effect between MoO₂ and MoP during the ECO of PX. So far, great progress has been made in the ECO of benzyl alcohols to benzyl acids in alkaline systems [54,55]. However, the electrochemical synthesis of benzyl acids from benzyl aromatics is still a huge challenge because the carboxyl group is easier to be oxidized relative to the methyl C-H bond. In this work, it is the first report on the direct ECO of benzyl aromatic methyl groups to benzyl acids with high selectivity in an alkaline media.

3.3. Potential-driven surface reconstruction of MoO₂/MoP precatalyst

Potential-dependent Raman spectra were collected in a three-electrode electrochemical cell to provide deep insights on the surface reconstruction of MoO₂/MoP/NF electrodes during ECO of PX. As shown in Fig. 5a, only a small peak at 744 cm⁻¹ attributed to the Mo-O stretching vibration of MoO₂ is detectable at the electrode surface without applied potential [43]. At 0.9 V, a new peak assigning to the ν₄ asymmetric stretching of MoO₄²⁻ appears at 316 cm⁻¹. With progressively increasing the applied potentials, the peak at 744 cm⁻¹ becomes insignificant, while new peaks belonging to the Mo-O-Mo bending vibration, ν₂ asymmetric stretching of MoO₄²⁻ and ν₄ asymmetric stretching of MoO₄²⁻ occur at 471, 833 and 891 cm⁻¹ respectively [56–58]. Meanwhile, the band at 1065 cm⁻¹ corresponding to the ν₃ triply degenerated asymmetric mode of P-O bond becomes obvious [23]. The above-mentioned changes of typical Raman peaks demonstrate the simultaneous formation of MoO₄²⁻ and PO₄³⁻ with the potential applied. All the characteristic bands exhibit the strongest intensities at 1.3 V,

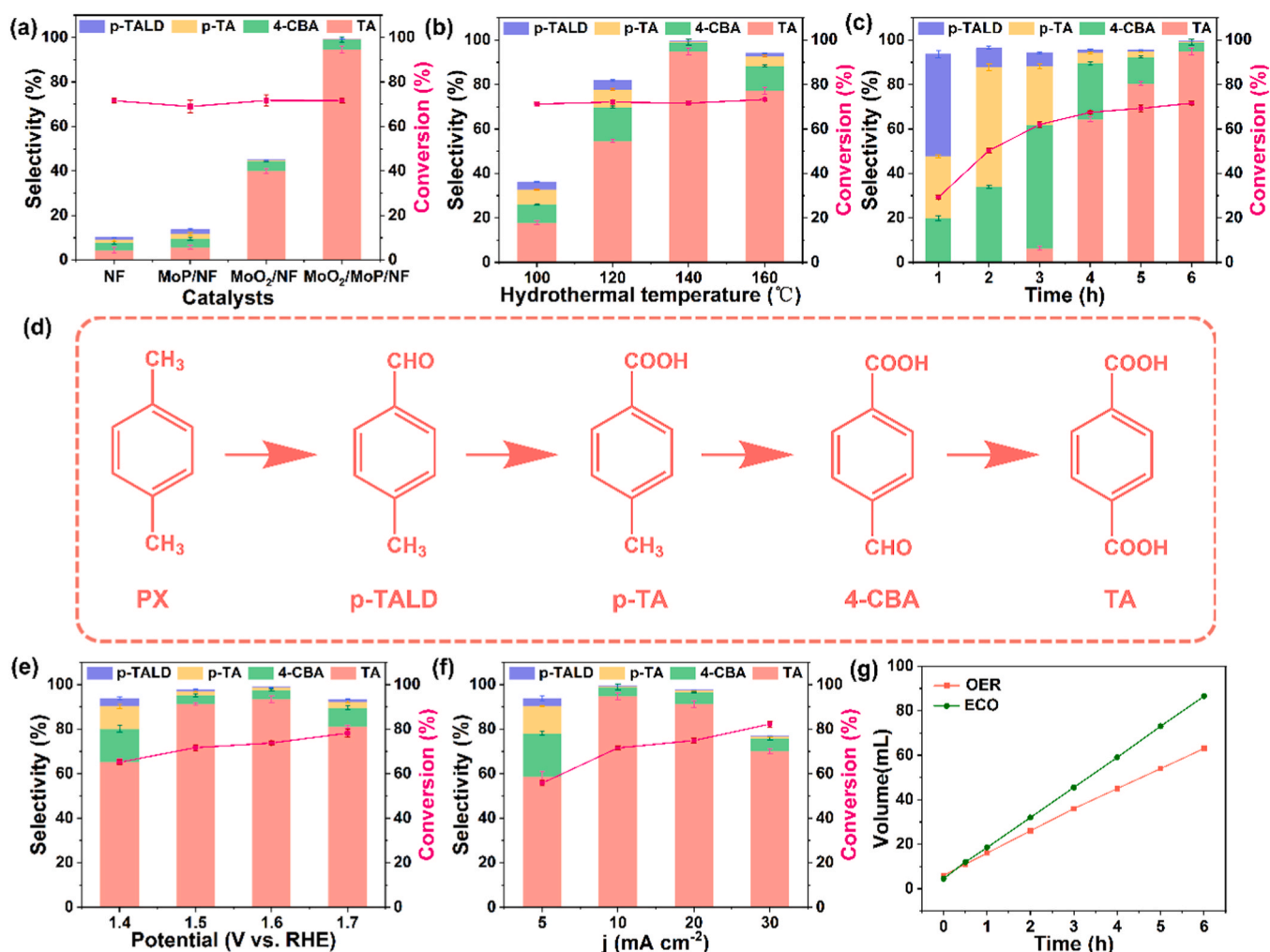


Fig. 3. (a) ECO of 25 mM PX over NF, MoP/NF, MoO₂/NF and MoO₂/MoP/NF electrodes for 6 h at 10 mA cm⁻². (b) ECO of 25 mM PX over MoO₂/MoP/NF-x electrodes for 6 h at 10 mA cm⁻². (c) Effect of reaction time on ECO of 25 mM PX over MoO₂/MoP/NF-140 at 10 mA cm⁻². (d) Reaction pathway for ECO of PX. (e) Effect of applied potential on ECO of PX over MoO₂/MoP/NF-140 for 6 h. (f) Effect of current density on ECO of 25 mM PX over MoO₂/MoP/NF-140 for 6 h. (g) Amount of hydrogen as a function of reaction time under ECO (with 25 mM PX) and OER (without PX) conditions over MoO₂/MoP/NF-140.

suggesting a complete surface reconstruction of the original electrode. Evidently, low valence Mo species in both MoP and MoO₂ undergo an anodic oxidation to form molybdate groups, while P species in MoP are also oxidized into phosphate groups during the ECO of PX. As a control, potential-dependent Raman spectra of the MoO₂/NF electrode was shown in Fig. 5b. The electrode surface of MoO₂/NF exhibit three typical peaks at 461, 496 and 746 cm⁻¹ assigned to MoO₂. Under the applied potential, the features of MoO₂ disappear. In the meanwhile, the peaks corresponding to MoO₄²⁻ and Mo-O-Mo gradually rise with the applied potential. This proves that MoO₂ also transforms into molybdate during the ECO process.

XRD and XPS were conducted to examine the surface structure of MoO₂/MoP/NF-140 after potential-induced surface reconstruction. As shown in Fig. 5c, two crystalline phases of orthorhombic MoP₂O₈ (PDF#16-0214) and triclinic K₂Mo₂O₇ (PDF#36-0347) can be observed after 2 h of reaction [59]. As the reaction time prolongs, the characteristic bands of both monoclinic MoO₂ and hexagonal MoP gradually disappear, whereas the diffraction features of both orthorhombic MoP₂O₈ and triclinic K₂Mo₂O₇ phases become more pronounced. At 6 h, the sample contains mixed crystalline phases of orthorhombic MoP₂O₈ and triclinic K₂Mo₂O₇, proving that MoO₂ and MoP transform to MoP₂O₈ and K₂Mo₂O₇. Based on the analysis of crystallite size, the MoP phase of as-synthesized MoO₂/MoP/NF disappears within 2 h of reaction, accompanied by the occurrence of the MoP₂O₈ phase. Moreover,

the crystallite size of MoP₂O₈ gradually increases as the reaction time prolongs. In the meanwhile, the crystallite size of MoO₂ phase progressively decreases while the mean size of K₂Mo₂O₇ significantly increases as ECO proceeds. This verifies a gradual transformation of physical phase during ECO process (Table S9). In addition, XRD pattern of post MoO₂/NF (Fig. S28) indicates the conversion of MoO₂ to K₂Mo₂O₇ during ECO process. Obviously, the K₂Mo₂O₇ phase generated from surface reconstruction of MoO₂/NF exhibits significant peaks at 24.4°, 26.9°, 28.7°, 36.4°, 42.1° and 53.3° corresponding to (111), (210), (-211), (2-11), (23-1) and (041) planes, which are different from the main crystal planes of K₂Mo₂O₇ converted from MoO₂/MoP/NF-140.

The high-resolution Mo 3d spectrum demonstrates that both MoP and Mo(IV) species in the as-synthesized electrode are oxidized into Mo(VI) species (Fig. 5d). The O 1s spectrum can be fitted into two B.E.s derived from Mo(VI)-O and P-O bonds, respectively (Fig. 5e). Moreover, the appearance of P-O bond indicates the oxidation-induced transformation of Mo-P into Mo-P-O (Fig. 5f) [31,46,60]. It is worth noting that the B.E.s for K 2p and K 2s are detectable for the post electrode (Fig. S29), further confirming the formation of K₂Mo₂O₇ phase. It is evident that the electrode surface achieves the complete transformation of electronic states of Mo, O and P elements after 2 h of reaction. Nevertheless, MoO₂ and MoP completely convert to MoP₂O₈ and K₂Mo₂O₇ after ECO of 6 h, which could be ascribed to the reconstitution

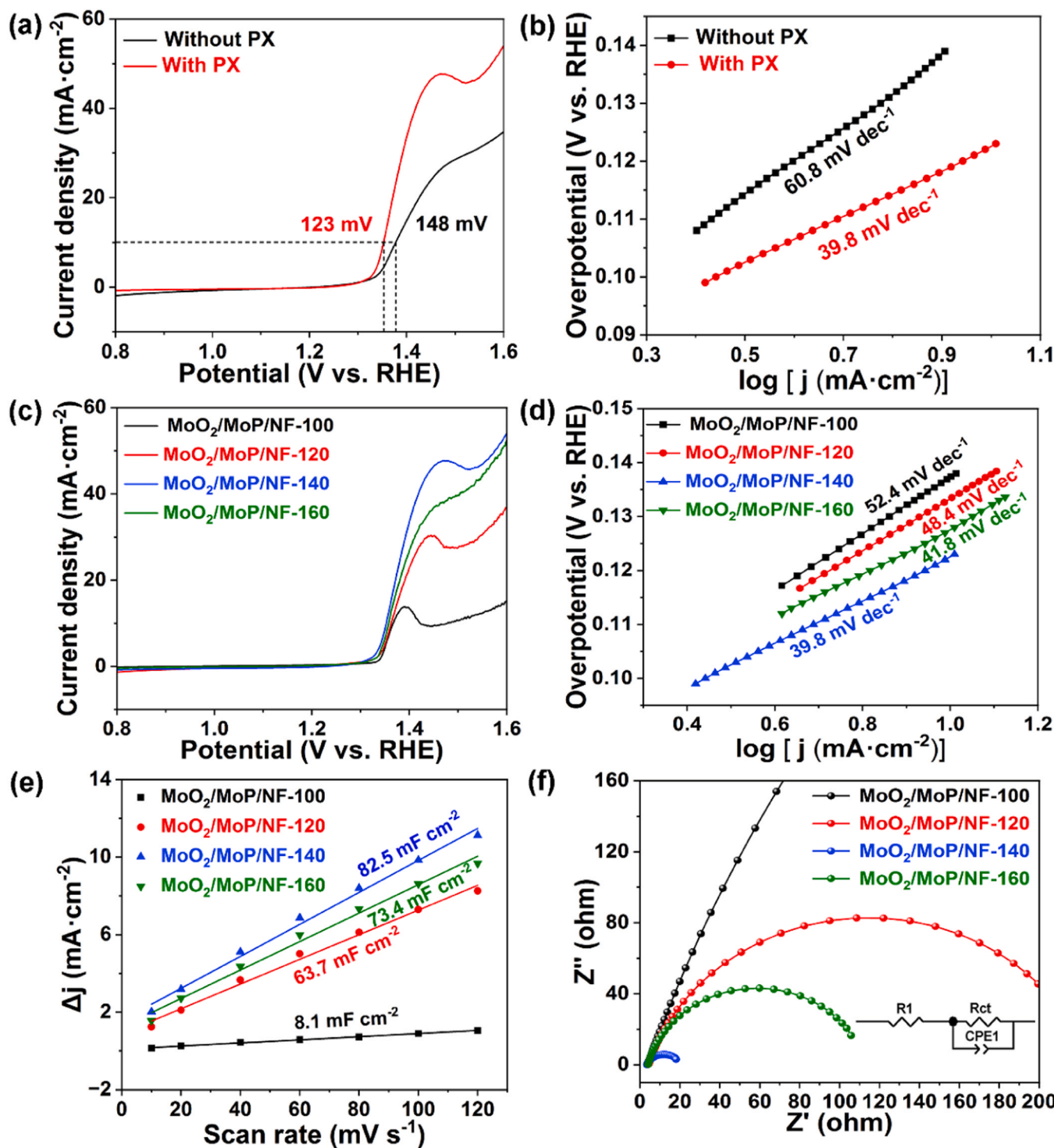


Fig. 4. (a) LSV curves, (b) Tafel slope plots of MoO₂/MoP/NF-140 in 1 M KOH containing 30% CH₃CN (V_{CH₃CN}: V_{H₂O} = 3/7) with and without PX. (c) LSV curves, (d) Tafel slope plots, (e) Double-layer capacitance (C_{dl}) and (f) EIS Nyquist plots of the MoO₂/MoP/NF-x electrodes in 1 M KOH containing 30% CH₃CN (V_{CH₃CN}: V_{H₂O} = 3/7) with 25 mM PX.

of bulk phase [31].

With prolonging the reaction time, the nanocone-covered surface becomes smooth (Fig. 6a-d). The MoO₂/MoP/NF-140 after ECO of 6 h presents the lattice spacing of 0.243 nm and 0.226 nm, which are consistent with the (202) crystal plane of MoP₂O₈ and the (32-1) plane of K₂Mo₂O₇, respectively (Fig. 6e-g) [59]. The SAED pattern comprises rings attributable to MoP₂O₈ and K₂Mo₂O₇ (Fig. 6h). For comparison, cluster-like morphology of MoO₂/NF-140 turns flat after reaction for 6 h

(Fig. S30). The lattice spacing for post MoO₂/NF-140 is in good agreement with the (2-11) plane of K₂Mo₂O₇ (Fig. S31).

Previous studies have reported that Mo-based anodic electrocatalysts are susceptible to be oxidized and leached to molybdate (MoO₄²⁻, K₂MoO₄ or K₂Mo₃O₁₀) in KOH during surface reconstruction [61]. These transformed molybdates can not only enhance the reconstruction degree of pre-catalyst into active phase, but also regulate the electronic conductivity of electrode material [62,63]. P species as pre-catalysts have

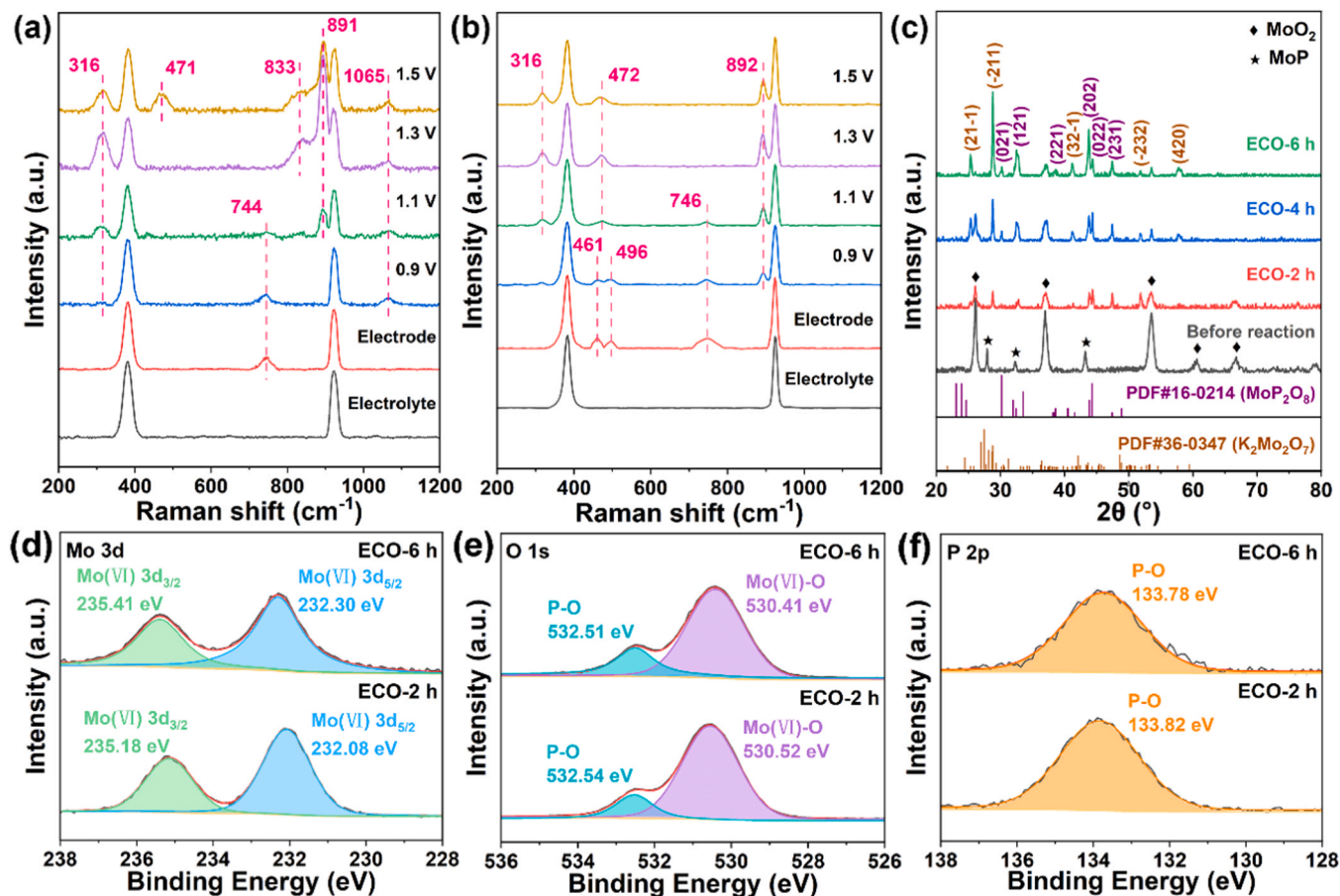


Fig. 5. In-situ Raman spectra of (a) MoO₂/MoP/NF-140 and (b) MoO₂/NF-140 in 1 M KOH containing 30% CH₃CN ($V_{\text{CH}_3\text{CN}}: V_{\text{H}_2\text{O}} = 3/7$) with 25 mM PX at different applied potentials (V vs. RHE). (c) XRD patterns of MoO₂/MoP/NF-140 after ECO at different reaction time. High-resolution XPS spectra for MoO₂/MoP/NF-140 after ECO: (d) Mo 3d, (e) O 1s, (f) P 2p.

also been demonstrated to form oxygen-rich phosphide and further leach to phosphates under anodic potential. The leached P species with etching effect can promote the lattice distortion, improve interfacial charge transfer as well as enhance active surface area [31,64]. In this study, the MoO₂/MoP hybrid undergoes a dynamic reconstitution to generate high-valent Mo species and P species. Partial leached Mo species form molybdate phase (K₂Mo₂O₇) in KOH electrolyte, whereas the rest of Mo and P species are co-reconstructed to produce phosphomolybdate phase (MoP₂O₈).

3.4. Reaction mechanism for ECO of PX

DFT calculations were performed to unveil the reaction mechanism for ECO of PX over reconstructed MoP₂O₈ and K₂Mo₂O₇ phases. According to XRD and HRTEM analysis (Figs. 5c, 6f-g), the (202) crystal plane of MoP₂O₈ and the (32-1) crystal plane of K₂Mo₂O₇ were selected to represent the surface structure of MoO₂/MoP after potential-driven reconstitution (Fig. S32). It is widely reported that the proton of methyl group of PX is easily abstracted by hydroxyl radicals to form p-methylbenzyl radicals (C₇H₇CH₂·) on the catalyst surface in PX-CH₃CN-H₂O system [65,66]. Consequently, the adsorption energy of C₇H₇CH₂· on the (202) plane of MoP₂O₈ and (32-1) plane of K₂Mo₂O₇ were calculated respectively. The C₇H₇CH₂· radical adsorbs on MoP₂O₈ via top oxygen sites (Fig. S33) with the adsorption energy of -2.37 eV (Fig. 7a). However, the adsorption energy of C₇H₇CH₂· adsorbed on K₂Mo₂O₇ via top oxygen sites is only -1.70 eV (Table S10), which is much lower than that on MoP₂O₈. Further, the adsorption energies of different intermediates and products on MoP₂O₈ were compared. The

p-TALD (-0.44 eV), p-TA (-0.56 eV) and 4-CBA (-0.48 eV) prefer to adsorb on MoP₂O₈ with the formyl groups located on top P sites (Fig. S34), whereas TA adsorbs weakly on MoP₂O₈ (-0.13 eV). It is suggested that TA is liable to desorb from the catalyst surface (Table S11).

In order to elucidate the critical role of P, the adsorption energies of different intermediates and products on the (2-11) crystal plane of K₂Mo₂O₇ (the dominant crystal plane for post MoO₂/NF) were also calculated (Fig. 7b, Table S12). All the intermediates and products are strongly adsorbed on the (2-11) plane of K₂Mo₂O₇ between Mo sites and methylene or formyl groups (Fig. S35). Accordingly, the strong adsorption between TA and Mo makes it difficult to desorb from the catalyst surface, which would lead to an over-oxidation of TA. Hence, it can be reasonably concluded that the doping of P can significantly reduce the adsorption of TA (-1.43 eV to -0.13 eV, Fig. 7c-d) and effectively improve the selectivity.

XPS analysis demonstrates that the MoO₂/MoP/NF-140 contains the highest proportion of MoP (Table S3). From the ECO results, the MoO₂/MoP/NF-140 exhibits considerably higher TA selectivity (94.8%) as compared to MoO₂/MoP/NF-100 (17.8%), MoO₂/MoP/NF-120 (54.6%) and MoO₂/MoP/NF-160 (77.3%), indicating that high proportion of MoP is favorable for high selectivity of TA. DFT calculations demonstrate that the top P site on the phosphomolybdate surface facilitates the adsorption of reaction intermediates but weakens the adsorption of TA. Therefore, MoO₂/MoP/NF-140 with the highest content of MoP may lead to abundant P sites on catalyst surface, thus effectively improving the selectivity of TA.

The catalytic mechanism for ECO of PX is proposed in Fig. 7e. The

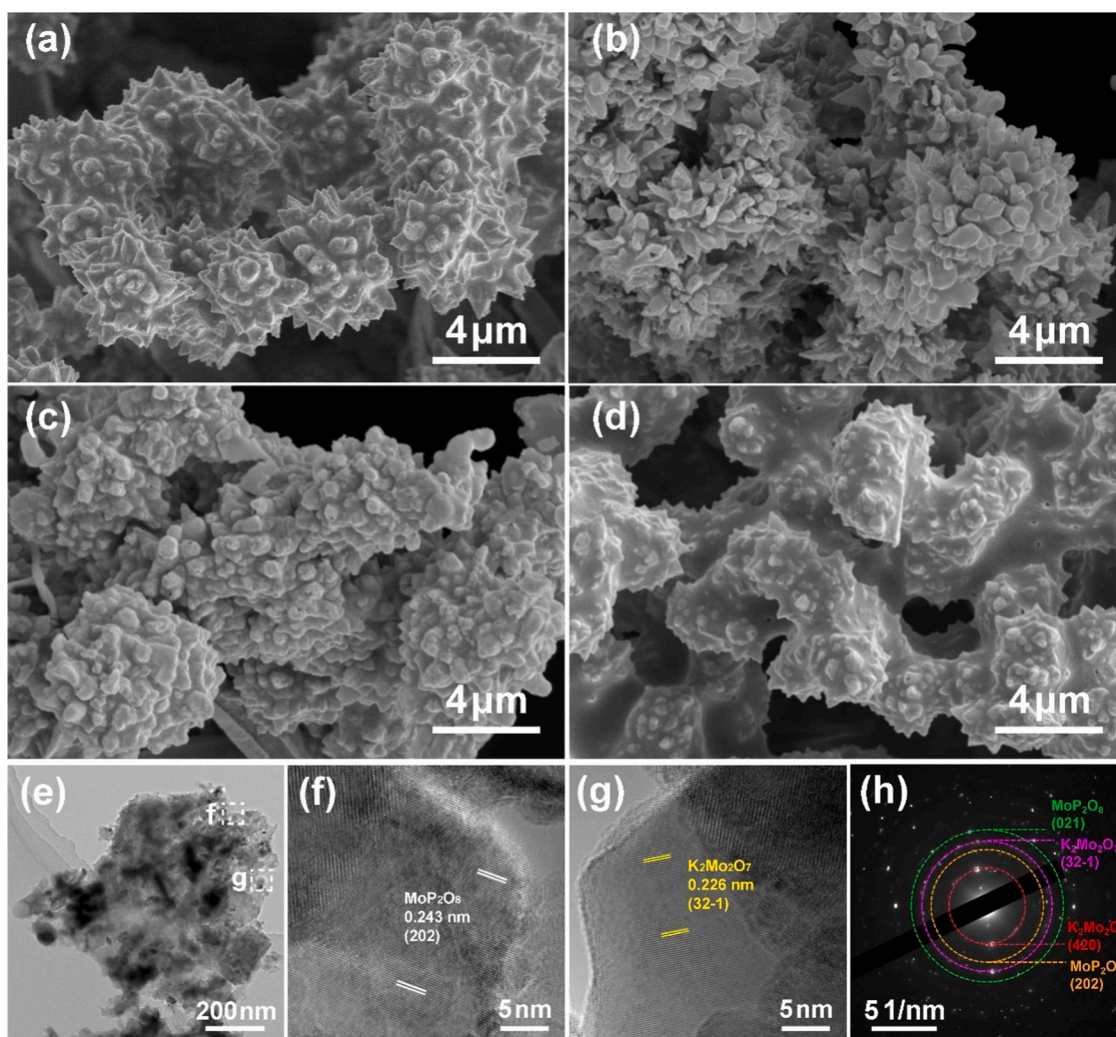


Fig. 6. SEM images of MoO₂/MoP/NF-140 before (a) and after reaction for (b) 2 h, (c) 4 h, (d) 6 h. (e) TEM image, (f, g) HRTEM images and (h) SAED pattern of MoO₂/MoP/NF-140 after reaction for 6 h.

surface of MoO₂/MoP/NF derives into MoP₂O₈ and K₂Mo₂O₇ phases via potential-induced surface reconstruction. Initially, the methyl group of PX undergoes a hydrogen abstraction to form C₇H₇CH₂· radical. The MoP₂O₈ surface modulates the adsorption strength of reaction intermediates involving p-TALD, p-TA and 4-CBA, mainly through the top P sites. Furthermore, it also weakens the adsorption strength of TA on the electrode surface, thereby facilitating the desorption of TA. For comparison, the MoO₂/NF without P doping converts to K₂Mo₂O₇ phase driven by electrochemical oxidation. Both reaction intermediates and oxidized product exhibit strong adsorption strength on the electrode surface via Mo sites, giving relatively low selectivity toward TA.

4. Conclusion

In summary, a facile hydrothermal-phosphorylation method was developed to fabricate hybrid MoO₂/MoP/NF electrode materials for ECO of PX in alkaline environment. The crystalline structures and morphologies of MoO₂/MoP precatalysts are highly dependent upon hydrothermal temperatures. The optimal electrocatalyst exhibits nanocone cluster-like architecture, resulting in outstanding electrochemical performance during ECO of PX such as large electrochemical surface area, highly exposed active sites and rapid charge transfer kinetics during ECO of PX. The ECO of PX gives the TA selectivity of 94.8% and faradaic efficiency of 76.9% at the PX conversion of 71.6%. As compared to OER process, the anodic oxidation of PX promotes the cathodic

hydrogen production by 30%. Moreover, PX electro-oxidation assisted water electrolysis requires only 1.42 V to drive 10 mA cm⁻² with a superior stability over 40 h. *In-situ* Raman and DFT calculations unravel the dynamic surface reconstruction of MoO₂/MoP/NF pre-catalyst during ECO of PX. New crystalline phases of MoP₂O₈ and K₂Mo₂O₇ simultaneously form during potential-driven *in-situ* reconstitution of MoO₂/MoP pre-catalyst. The top P sites on the (202) plane of MoP₂O₈ adjust the adsorption energies of p-TALD, p-TA and 4-CBA. The MoP₂O₈ surface also weakens the adsorption strength of TA, thereby contributing to high selectivity. For comparison, electrocatalytically generated K₂Mo₂O₇ phase on the MoO₂/NF without P doping shows low selectivity probably due to large adsorption energy of TA on the dominant crystal plane. This work clarifies the role of P element of transition-metal phosphide during ECO of organic compounds and opens up a new path to explore the real active sites of electrocatalysts for valuable chemicals production via potential-induced surface reconstruction.

CRediT authorship contribution statement

Ye Lv: Methodology, Investigation, Writing – original draft. **Mao Peng:** Software, Density functional theory (DFT) calculations. **Weiwei Yang:** Methodology, Investigation. **Menghui Liu:** Visualization. **Aiqun Kong:** Methodology, Data curation. **Yan Fu:** Conceptualization, Writing – review & editing. **Wei Li:** Resources, Supervision, Writing – review & editing. **Jinli Zhang:** Project administration, Funding acquisition,

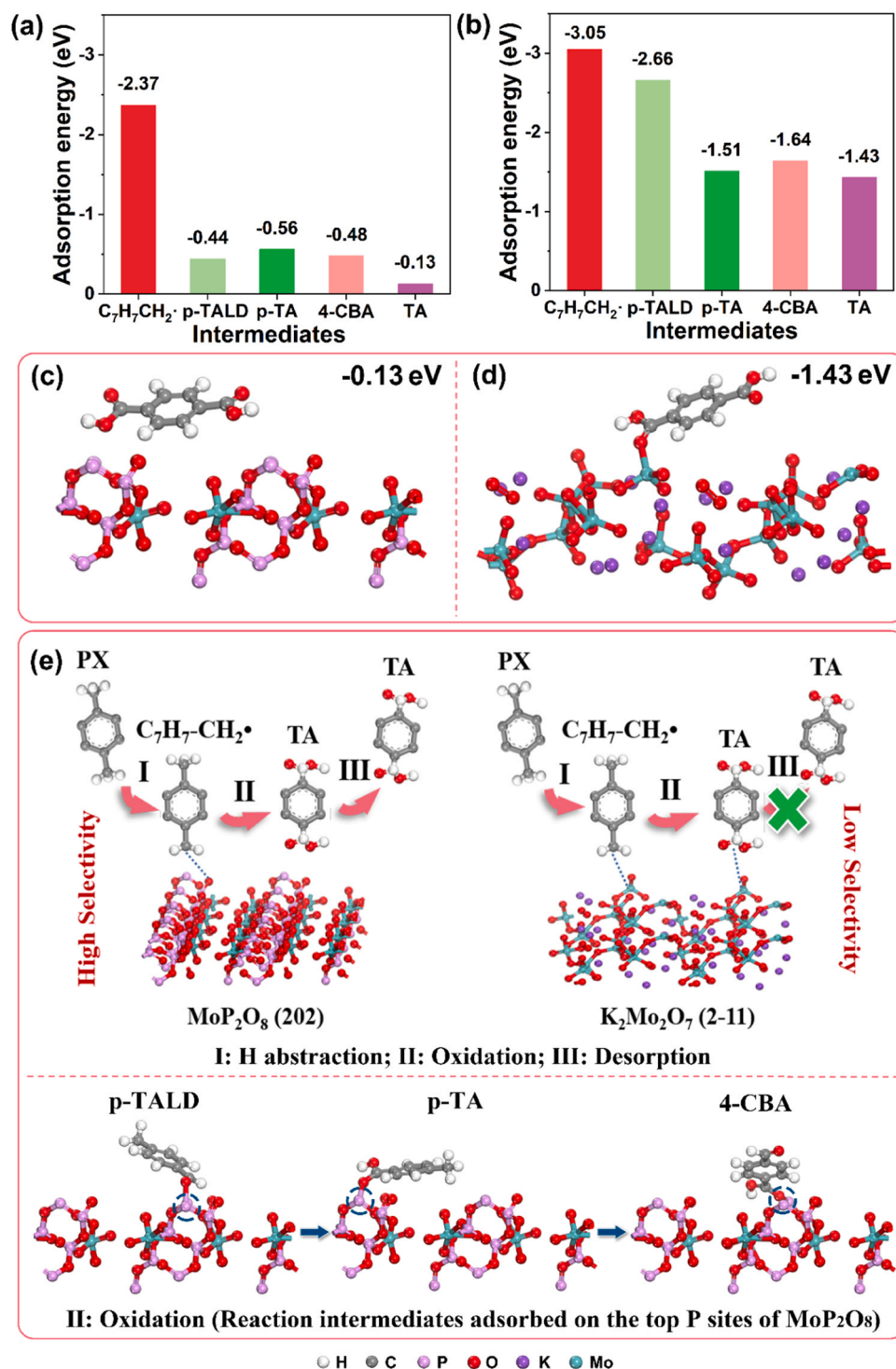


Fig. 7. The adsorption energies (eV) of different intermediates on (a) the (202) crystal plane of MoP₂O₈, (b) the (2–11) crystal plane of K₂Mo₂O₇. Ball and stick model of adsorption of TA on (c) the (202) crystal plane of MoP₂O₈, (d) the (2–11) crystal plane of K₂Mo₂O₇. (e) Illustration of the mechanism for ECO of PX.

Writing – review & editing. All authors have read and agreed to the published version of the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

Acknowledgments

This work was financially supported by NSFC (No. 22090034, U20A20151), the National Key Research and Development Program (2021YFB4000303).

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.apcatb.2023.123229](https://doi.org/10.1016/j.apcatb.2023.123229).

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